

Enhanced electrocatalytic activity and stability of PdCo@Pt core-shell nanoparticles for oxygen reduction reaction

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Abstract The carbon-supported PdCo@Pt core-shell nanoparticles for an oxygen reduction reaction (ORR) were prepared via a two-step process at room temperature. The as-prepared PdCo@Pt/C with an average particle size of ~ 3.5 nm exhibited a well-defined nanostructure consisting of Pd-rich core and Pt shell formed by displacing Co core with Pt. Compared to pure Pt, PdCo@Pt/C showed a higher current density in the kinetic controlled region and more positive half-wave potential for the ORR. In a cycling stability test of the PdCo@Pt/C electrocatalyst, no remarkable activity loss was seen.

Keywords Core-shell · PdCo@Pt · Electrocatalyst · Oxygen reduction reaction

1 Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have been a promising electrochemical power source because of their high energy efficiencies, reduced pollution emissions, and low operating temperatures [1–3]. However, the kinetically sluggish oxygen reduction reaction (ORR) at the cathode, where oxygen, as the oxidant, is reduced into water by reaction with protons and electrons, limits the electrochemical energy efficiency of PEMFCs [4]. The slow kinetics of the ORR remains a serious challenge for mass

production of PEMFCs, because they require high Pt loading at the cathode [5–7].

Abruña and co-workers suggested a simple synthesis of PdCo@Pd core-shell nanoparticles (NPs) supported on carbon using an adsorbate-induced surface segregation effect. The stability of PdCo@Pd NPs and their electrocatalytic activity for the ORR were enhanced by decoration with a small amount of Pt deposited via a spontaneous displacement reaction [8, 9]. Adzic and co-workers reported that a synthesis of electrocatalysts with well-defined core-shell structure has been carried out via a galvanic displacement and an underpotential deposition. The as-prepared Pd₂Co@Pt/C core-shell electrocatalyst with an average particle size of ~ 5.4 nm with a broad size distribution showed excellent ORR activity and stability in an accelerated potential cycling test [10–12]. Liu et al. [13] represented bimetallic Pt–Pd core-shell NPs such as Pd(core)@Pt(shell)/C and Pt(core)@Pd(shell)/C synthesized by co-reduction and sequential reduction methods in ethylene glycol (EG).

Herein, we demonstrate a facile method of carbon-supported PdCo@Pt core-shell NPs as ORR electrocatalysts prepared via a two-step route at room temperature [14–19]. The structure, morphology, and composition of the carbon supported NPs are characterized by transmission electron microscopy (TEM), energy-dispersive spectroscopy (EDS), and X-ray diffraction method (XRD). Electrochemical characterizations are carried out with cyclic voltammograms (CVs) and linear sweep voltammetry (LSV) with a rotating disk electrode.

2 Experimental

We synthesized carbon supported PdCo@Pt NPs prepared via a two-step route. First, PdCo₃ as a core deposited on

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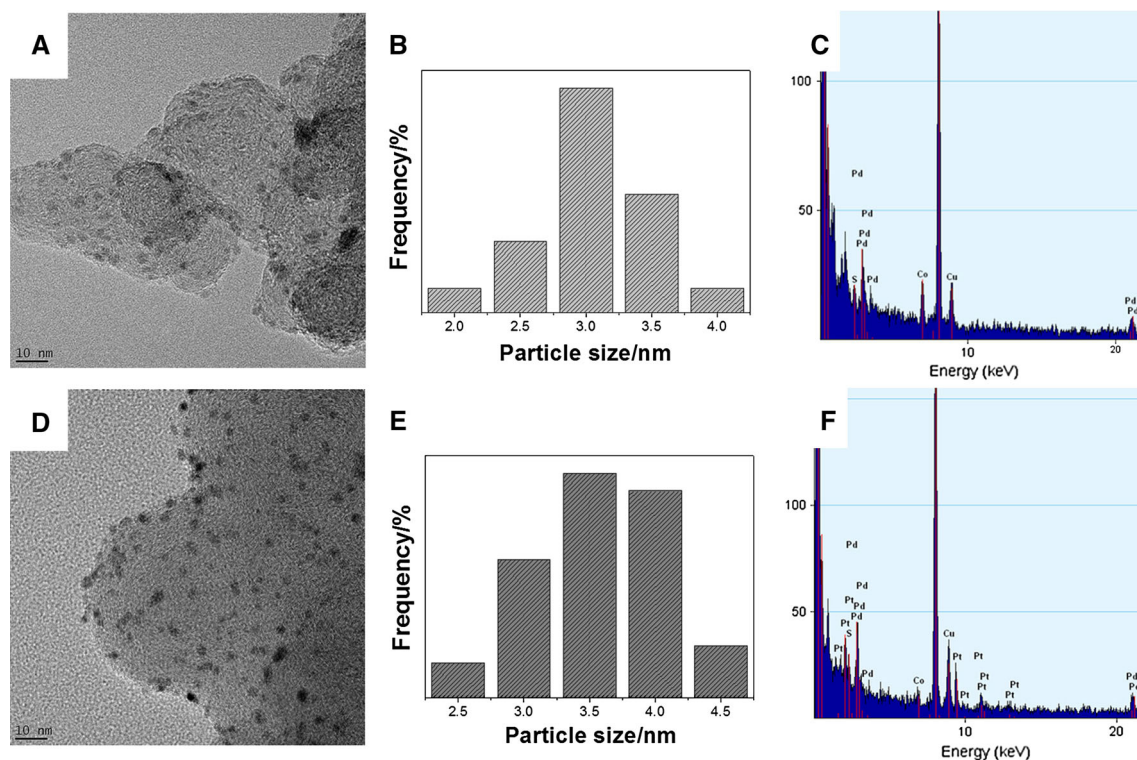


Fig. 1 TEM images (a), histogram of size distribution (b), and EDS data (c) of PdCo/C as a core. TEM images (d), histogram of size distribution (e), and EDS data (f) of PdCo@Pt/C as an electrocatalyst

carbon black was synthesized by NaBH_4 reduction in anhydrous ethanol (99.5 %, Sigma Aldrich). Sodium tetrachloropalladate (29.7 mg, Na_2PdCl_4 , Sigma Aldrich) and cobalt chloride hexahydrate (72.3 mg, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, Sigma Aldrich) were dispersed in 100 mL of anhydrous ethanol with carbon black (113 mg, Vulcan XC-72R). After stirring and sonicating the mixture solution for 1 h, 75.7 mg of sodium borohydride (NaBH_4 , Sigma Aldrich), as a reducing agent in 10 mL of anhydrous ethanol, was quickly added to the mixture solution with continuous sonication. Second, for the electrocatalyst PdCo@Pt/C, the as-synthesized PdCo/C was redispersed in 100 ml of anhydrous ethanol. The pH of the dispersion solution was adjusted to ~ 7 by adding 10 mL of 2 M NaOH in anhydrous ethanol to stabilize the PdCo as a core. 1 mM of chloroplatinic acid hydrate (H_2PtCl_6 , Sigma Aldrich) in EG as a stabilizer was added in the mixture solution. In the mixture solution, PdCo@Pt/C was formed by a galvanic displacement reaction in EG at 25 °C for 24 h. The resulting powder was washed with water and then dried at 50 °C in an oven for 12 h.

XRD patterns of PdCo@Pt/C were obtained using a Bruker D2 PHASE system with Cu K_α source ($\lambda = 0.15$, 406 nm) radiation at 30 kV and 10 mA between 20° and 80°. The size, morphology, and composition of the catalysts were analyzed by TEM using an FEI Tecnai F30

system operated at 300 kV and EDS combined with the TEM analysis. TEM samples were prepared by placing drops of catalyst suspension dispersed in ethanol on a carbon-coated copper grid. The weight ratio of metallic elements was confirmed by inductively coupled plasma-atomic emission spectrometer (ICP-AES, Optima-4,300 DV, Perkin Elmer).

The electrocatalytic properties were measured in a three-electrode cell using a potentiostat (Metrohm Autolab, PGSTAT302) at room temperature. Pt wire and Hg/HgO (in saturated 1 M NaOH) were used as the counter and reference electrode, respectively. The glassy carbon as a working electrode was coated with 5 μL of catalyst ink prepared by mixing catalyst (10 mg), deionized water, isopropyl alcohol, and 5 wt % As-4 (TOKUYAMA). After drying in an oven at 50 °C, the total loading of catalyst was 20 $\mu\text{g}_{\text{metal}} \text{cm}^{-2}$. CVs of the samples were obtained in Ar-purged 0.1 M NaOH at 50 mV s^{-1} at room temperature. The ORR polarization curves of the samples were obtained in O_2 -saturated 0.1 M NaOH with 1,600 rpm and 5 mV s^{-1} .

3 Results and discussion

Figure 1 shows PdCo/C as a core prepared by NaBH_4 reduction in anhydrous ethanol and PdCo@Pt/C as an

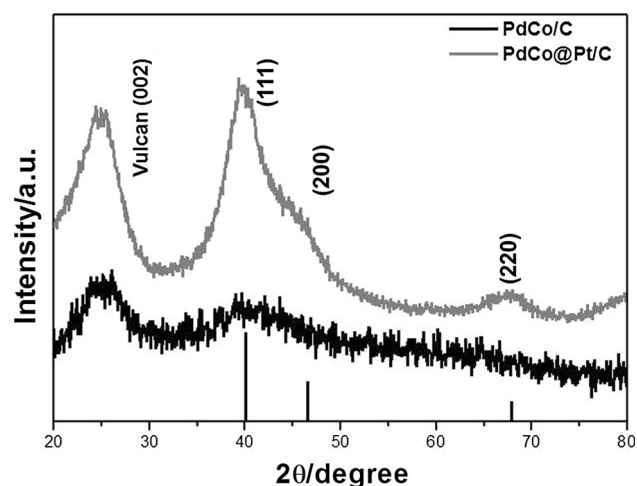


Fig. 2 XRD patterns of PdCo/C and PdCo@Pt/C in comparison with XRD reference data of Pd (JCPDS No. 88-2335)

electrocatalyst formed by a galvanic displacement reaction in EG. As indicated in Fig. 1a and b, PdCo/C exhibits the well-dispersion of PdCo NPs with an average particle size of ~ 3.0 nm and atomic ratio of Pd:Co = (36.4:63.6). Through the galvanic displacement process of PdCo/C, PdCo@Pt/C represents core-shell NPs with an average particle size of ~ 3.5 nm and atomic ratio of Pd:Co:Pt = (67.7:4.4:27.9) (Fig. 1C). The increased particle size and variation of composition of PdCo@Pt/C, compared to PdCo/C, indicate a well-defined nanostructure with a Pd-rich core and a Pt shell formed by displacing the Co core by Pt at room temperature. As indicated in the XRD results for the samples (Fig. 2), PdCo/C exhibits characteristic patterns for the face-centered-cubic structure of Pd. The diffraction peaks for PdCo@Pt/C remained at the same 2θ positions as found for PdCo/C, suggesting that Pt overlayers are formed on top of the PdCo NPs.

The CVs of the samples in Ar-saturated 0.1 M NaOH are shown in Fig. 3a. The as-prepared PdCo@Pt with a very small size is hard to analyze the mapping or line-profile analysis by TEM. However, as shown in Fig. 3a, the oxygen reduction peak of PdCo@Pt/C shifts to a higher potential by 0.14 mV in comparison with PdCo/C, indirectly implying a formation of Pt shell on PdCo core structure. Especially, in hydrogen desorption regions of CVs for the NPs (Fig. 3b), PdCo@Pt/C exhibits typical electrochemical characteristics of polycrystalline Pt similar to those of Pt/C (E-TEK Co.) compared to PdCo/C as a core, indicating the complete surface displacement by Pt for PdCo@Pt/C. The electrochemical active surface area of the PdCo@Pt/C is ~ 76.7 m 2 g $^{-1}$, exhibiting 2.4-fold enhancement compared to that of Pt/C (~ 32.1 m 2 g $^{-1}$).

Figure 4a–c displays the ORR polarization curves for the samples in O $_2$ -saturated 0.1 M NaOH, using a rotating

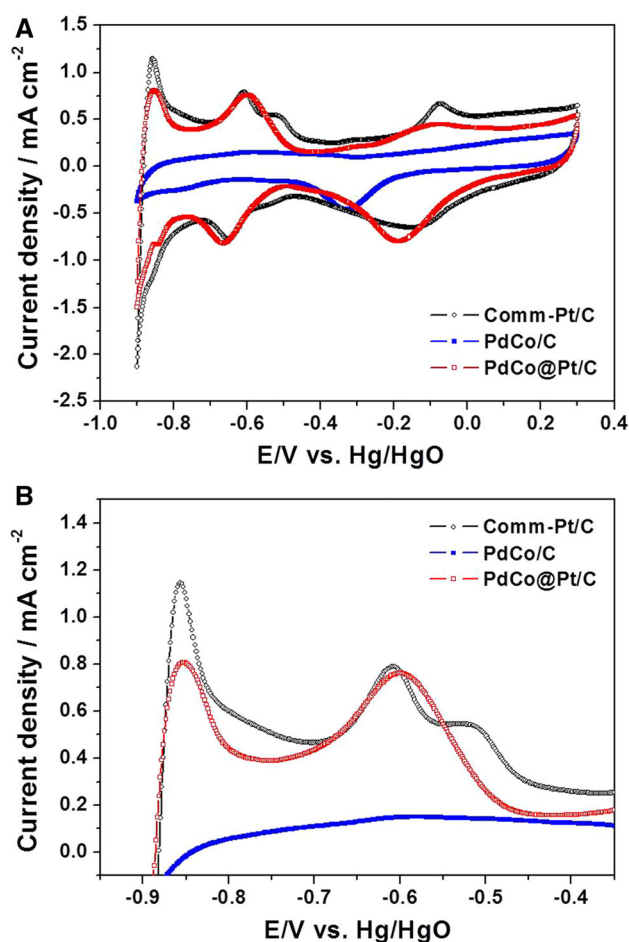


Fig. 3 CVs (a) of PdCo/C and PdCo@Pt/C and hydrogen oxidation regions (b) of PdCo/C, PdCo@Pt/C, and Comm-Pt/C in Ar-saturated 0.1 M NaOH with a scan rate of 50 mV s $^{-1}$ at room temperature

disk electrode (RDE) at 1,600 rpm at room temperature before and after stability. The current density was normalized to the geometric surface area of the electrodes. The PdCo@Pt/C showed higher ORR current density of -0.410 mA cm $^{-2}$ at 0.05 V i.e. the kinetic controlled region, and more positive half-wave potential of -0.016 V, compared to Pt/C. The area-based current densities (j_{area}) of the PdCo@Pt/C and Pt/C catalysts at 0.05 V are 0.097 and 0.060 mA cm $^{-2}$, respectively. Furthermore, the kinetic current density (j_k) of the PdCo@Pt/C, PdCo/C, and Comm-Pt/C is 0.447, 0.074, and 0.418 mA cm $^{-2}$ at -0.85 V, respectively. Also, the electron transfer numbers (n) of as-prepared catalysts were calculated on the basis of Koutecky-Levich plots as shown in Fig. 5. The n value for the PdCo@Pt/C toward ORR is ~ 4.0 , which shows improved electrochemical activity compared to Comm-Pt/C (~ 3.8). The enhancement of the ORR activity for PdCo@Pt/C might be attributed to the lower oxygen binding energy on a Pt shell of PdCo@Pt/C than that on pure Pt [20].

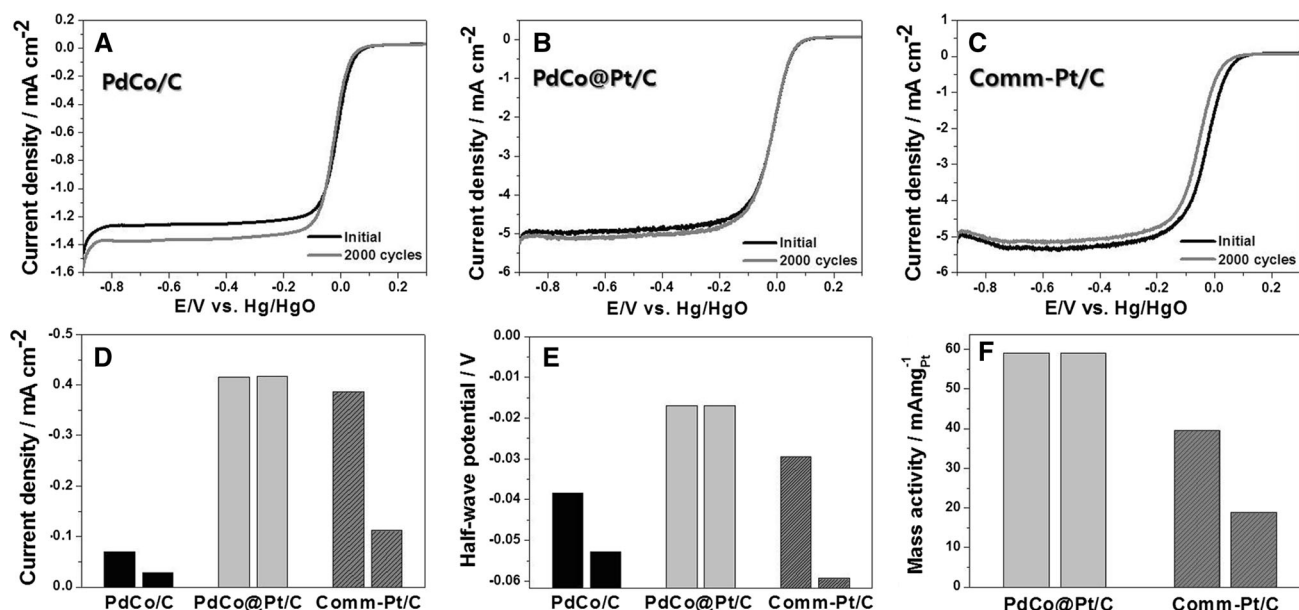


Fig. 4 ORR polarization curves (a–c) for the samples before and after the stability test in O₂-saturated 0.1 M NaOH solution, 1,600 rpm, 5 mV s⁻¹. The stability test of the samples was performed by sweeping between –0.3 and 0.1 V for 2,000 cycles at room

temperature. Comparison of ORR current density (d), half-wave potential (e), and mass activity (f) for the samples at 0.05 V before and after the stability test

To confirm the long-term stability of the electrocatalysts, the stability test was performed by cycling between –0.3 and 0.1 V for 2,000 cycles in O₂-saturated 0.1 M NaOH (Fig. 4a–c) [20]. As shown in Fig. 4d–f, PdCo@Pt/C exhibits no remarkable current density loss and no degradation in the half-wave potential for the ORR after the cycling stability test compared to Pt/C, representing much enhanced ORR stability of PdCo@Pt/C as an electrocatalyst.

4 Conclusions

We have demonstrated the carbon supported PdCo@Pt core–shell NPs prepared via a two-step route. The core–shell NPs were synthesized by coreduction of PdCo/C as a core and a galvanic displacement reaction for PdCo@Pt/C. The as-prepared PdCo@Pt/C electrocatalyst with a core–shell structure showed much improved electrochemical properties such high specific mass and kinetic activity, and enhanced stability in oxygen reduction reaction.

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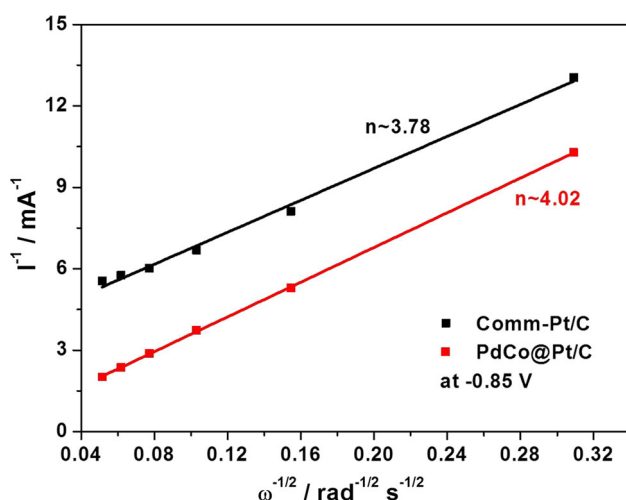


Fig. 5 Koutecky-Levich plots of PdCo@Pt/C and Comm-Pt at –0.85 V

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